

A Study of the Perchlorates of the Alkali and Alkaline Earth Metals, Their Preparation, Solubilities, and Use in Quantitative Analysis

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN THE UNIVERSITY OF MICHIGAN

By

G. Frederick Smith

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G. FREDERICK SMITH

Ann Arbor, Michigan

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A STUDY OF THE PERCHLORATES OF THE ALKALI AND ALKALINE EARTH METALS, THEIR PREPARATION, SOLUBILITIES, AND USE IN QUANTITATIVE ANALYSIS

Introduction

The work done in connection with this paper deal with the perchlorates of barium, strontium, calcium, magnesium, lithium, sodium, potassium, rubidium, cesium and ammonium. Solubilities of the anhydrous perchlorates at 25° were determined in water and in anhydrous methyl, ethyl, n-propyl, iso- and n-butyl alcohols, ether, acetone and ethyl acetate. The solubility of lithium perchlorate trihydrate was also determined in the above solvents. In the study of these perchlorates a careful search was made for new hydrates and into the conditions for their preparation.

A study was made of the properties of anhydrous magnesium perchlorate and magnesium perchlorate trihydrate with relation to their use as dehydrating agents.

A study was also made of the use of alcoholic perchlorate solutions as a basis for a new procedure in the separation and determination of sodium and lithium. Other work of a nature similar to this type of analytical method is suggested.

History

The first general study of the metallic perchlorates was made by Serrullas¹ and dealt with the preparation of eighteen perchlorates including those of the alkali and alkaline earth metals. The study was mainly qualitative, the observation being made that, of the perchlorates studied, only those of potassium, rubidium and cesium were insoluble in water and alcohol. The solubility of potassium perchlorate in water was given.

Barium perchlorate trihydrate was prepared by O. Henry.² A hydrate of barium perchlorate, $\text{Ba}(\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$ was described by Marignac³ which was not confirmed by Potilitzin,⁴ who prepared and analysed the anhydrous salt, monohydrate and trihydrate of barium, perchlorate, the first by drying the hydrates over sulfuric acid at 100° the second by the same means at ordinary temperature and the last by crystallization from water at ordinary temperatures. It was found that anhydrous barium perchlorate was fairly stable up to 400° C. only 0.09% of its oxygen content

¹ Serrullas, *Ann. chin. phys.*, [2] **46**, 297 (1831).

² Henry, *J. Pharm.*, **25**, 268(1839).

³ Marignac, *Jahresbericht*, **1855** 342.

⁴ Potilitzin, *J. Russ. Phys. Chem. Soc.*, **19**, I, 339(1887).

being lost during seventy minutes at this temperature. The solubility of barium perchlorate in water at various temperatures was determined by Carlson.⁵

Magnesium perchlorate hexahydrate was prepared by Weinland and Ensgraber.⁶

No record of the solubilities of the perchlorates of strontium calcium and magnesium was found.

Lithium perchlorate trihydrate was studied by Wyruboff.⁷ A study of the preparation of lithium perchlorate in the anhydrous condition and as the di- and tri-hydrates was made by Potilitzin.⁸ He gave the melting point of the trihydrate as 95°, its decomposition to the monohydrate occurred at 95–100°. The monohydrate changed to the anhydrous salt at 130–150° and the melting point of the latter was given as 380°. A more exact record of the physical constants of anhydrous lithium perchlorate was made by Richards and Willard⁹ who found its density to be 2.4287 at 25°/4° and its first decomposition upon heating to occur at about 300°. After extreme purification the decomposition point was raised to 400°, as found by Richards and Cox.¹⁰ Potilitzin⁸ described the preparation of anhydrous sodium perchlorate and its monohydrate. The solubility of sodium perchlorate in water at various temperatures was given by Carlson.⁵

The solubility of potassium perchlorate in water has been determined by Louguinine,¹¹ Hutstein¹², Muir,¹³ Noyes and Sammet,¹⁴ Rothmund,¹⁵ Colzolari,¹⁶ Carlson,⁵ Noyes and Boggs,¹⁷ Thin and Cumming,¹⁸ and Stolba.¹⁹ The solubility of potassium perchlorate in different solution of water in alcohol was determined by Thin and Cumming.¹⁸ The solubility in alcohol was determined by Schlösing.²⁰ The solubility in alcohol, alcohol and ether mixtures and alcohol with perchloric acid was deter-

⁵ Comey-Hahn, *Dictionary of Solubilities*, 1921, 649; Festsck, *Stockholm*, 1911, 262.

⁶ Weinland and Ensgraber, *Z. Anorg. Allgem. Chem.*, **84**, 372 (1914).

⁷ Wyruboff, *Z. Kryst. Min.*, **10**, 625 (1885).

⁸ Potilitzin, *J. Russ. Phys. Chem. Soc.*, **1**, 258 (1889).

⁹ Richards and Willard, *J. Am. Chem. Soc.*, **32**, 4 (1910).

¹⁰ Richards and Cox, *J. Am. Chem. Soc.*, **36**, 819 (1914).

¹¹ Louguinine, *Ann.*, **121**, 123 (1862).

¹² Hutstein, *Jahresbericht*, **1851**, 331.

¹³ Muir, *Chem. News*, **33**, 15 (1876).

¹⁴ Noyes and Sammet, *Z. physik. Chem.*, **43**, 538 (1903).

¹⁵ Rothmund, *Ibid.*, **69**, 539 (1909).

¹⁶ Colzolari, *Acc. Sci. Med. Ferrara*, **85**, 150 (1911).

¹⁷ Noyes and Boggs, *J. Am. Chem. Soc.*, **33**, 1652 (1911).

¹⁸ Thin and Cumming, *J. Chem. Soc.*, **107**, 361 (1915).

¹⁹ Stolba, *Z. anal. Chem.*, **2**, 390 (1863).

²⁰ Schlösing, *Compt. Rend.*, **73**, 1269 (1871).

mined by Wenzel.²¹ The solubility in various organic solvents containing water was determined by Rothmund.¹⁵ Potassium perchlorate was found by Navmann to be insoluble in methyl acetate²² and ethyl acetate.²³ The solubility in methyl alcohol was determined by Baxter and Rupert²⁴ and in ethyl alcohol by Baxter and Kobayashi.²⁵ The solubility of rudibium perchlorate in water at various temperatures was determined by Carlson⁵ and Louguinine¹¹ and Erdmann²⁶ and Colzolari.¹⁶

The solubility of ammonium perchlorate in water was determined by Mitscherlich,²⁷ Thin and Cumming,¹⁸ Hofmann Höbold and Quoos,²⁸ and Carlson.⁵ The solubility in 98.8% alcohol was determined by Thin and Cumming.¹⁸ Ammonium perchlorate was found by Carbonelli²⁹ to be soluble in acetone.

It is evident therefore that very little work has been done upon the perchlorates of the alkali and alkaline earth metals with the exception of potassium.

Preparation of Materials

Perchloric Acid.—This was prepared by the method of Willard³⁰ and was twice distilled under a pressure of 5–15 mm. It contained 70–72.5% of perchloric acid and was free from non-volatile matter.

Calcium Perchlorate.—Pure calcium nitrate was twice recrystallized, using centrifugal drainage, and converted into the perchlorate by evaporation with excess of perchloric acid. The excess of acid was neutralized by pure calcium carbonate, prepared from the purified nitrate by precipitation with pure ammonium carbonate. The solution was centrifuged until a clear supernatant liquid could be decanted. This was then crystallized.

Calcium perchlorate contains 4 molecules of water of crystallization and melts below 100°. It was heated at a gradually increasing temperature until all crystal water was expelled and finally dried to constant weight at 250°. It was perfectly stable at 260–270°.

Some of the crystals were dried to constant weight in a desiccator over the anhydrous salt. Upon further heating to 250° the salt lost 23.11% of water; the theoretical value for the tetrahydrate is 23.15%.

Strontium Perchlorate.—Pure strontium nitrate was twice recrystal-

²¹ Wenzel, *Z. Angew. Chem.*, **23**, 691 (1891).

²² Navmann, *Ber.*, **42**, 3790 (1909).

²³ Navmann, *Ibid.*, **43**, 314 (1910).

²⁴ Baxter and Rupert, *J. Am. Chem. Soc.*, **42**, 2046, (1920).

²⁵ Baxter and Kobayashi, *J. Am. Chem. Soc.*, **39**, 249 (1917).

²⁶ Erdmann, *Arch. Pharm.*, **232**, 23 (1894).

²⁷ Mitscherlich, *Annalen der Physik und Chemie*, **25**, 300 (1833).

²⁸ Hofmann Höbold and Quoos, *Ann.*, **386**, 304 (1912).

²⁹ Carbonelli, *Chem. Abs.*, **4**, 3299 (1910).

³⁰ Willard, *J. Am. Chem. Soc.*, **34**, 1480 (1912).

lized and converted into perchlorate in the manner just described for the calcium salt. It was dried to constant weight at 250° .

When crystallized at about 0° , strontium perchlorate apparently contains 4 molecules of water, although the data on this point are only approximate. At about 25° a dihydrate is obtained (found, 11.19% of water; calc., 11.17%) and the crystals formed above 40° after drying for several days over the anhydrous salt contained 8.65% of water, corresponding to the formula, $3\text{Sr}(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$, which requires 8.62%. The transition point of $3\text{Sr}(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ to $\text{Sr}(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ was found to be approximately 37° . So pronounced is the tendency of the former salt to form supersaturated solutions that its solubility in water at 25° was determined without any separation of the stable phase.

When tristrontium-perchlorate dihydrate was dried over the anhydrous salt for 30 days, it showed a water content of 7.77% as compared with the original 8.62%. This indicates the possible existence of a monohydrate.

Barium Perchlorate.—Very pure barium chloride was evaporated with an excess of perchloric acid and the barium perchlorate thus obtained was recrystallized twice at about 25° . This removed all excess of acid. The crystals dried to constant weight over the anhydrous salt contained 5.04% of water; the dihydrate requires 5.08%. Other investigators have obtained the trihydrate by recrystallization from water. When the crystals are dried over sulfuric acid the monohydrate is obtained. The mono- and dihydrates when exposed to moist air until constant in weight, formed the trihydrate (found, 13.80% of water; calc., 13.85%). The latter, when heated gradually to 250° in a current of dry air, lost all of its water without melting. A sample of the anhydrous salt thus prepared, when heated at 400° for 2 hours, gave up no water to a weighed phosphorus pentoxide tube. It then contained 2.89% of barium chloride, resulting from the slight decomposition at this temperature.

Magnesium Perchlorate.—The preparation and properties of this material will be described in a subsequent section.

Lithium Perchlorate.—The preparation of the trihydrate and anhydrous salt will be described in a subsequent section.

Sodium Perchlorate.—The preparation of this salt will be described in a subsequent section.

Potassium Perchlorate.—Very pure potassium carbonate was neutralized with perchloric acid, recrystallized and dried at 250° .

Rubidium Perchlorate.—The rubidium nitrate available contained cesium which was removed in the following manner. To 40 g. of the nitrate dissolved in 300 cc. of water was added silicotungstic acid in excess of that required to precipitate the cesium,³¹ and the precipitate of cesium with some rubidium silicotungstate was filtered off, ammonium carbonate was added,

³¹ Codeffroy, *Ber.*, 9, 1363 (1876).

and the solution boiled to precipitate the silica, which was filtered off. The solution was acidified and evaporated to dryness to separate the tungstic acid. The residue was extracted with water, filtered, and the solution evaporated with an excess of perchloric acid. The rubidium perchlorate thus obtained was recrystallized and dried at 250°. It gave no spectroscopic indication of cesium.

Cesium Perchlorate.—A very pure sample of cesium chloride prepared from pollucite was kindly furnished by Mr. E. O. Scott. It was converted to perchlorate by evaporation with excess of perchloric acid, recrystallized and dried at 250°.

Ammonium Perchlorate.—Ammonia gas, from the action of sodium hydroxide on pure ammonium chloride, was passed into dil. perchloric acid. The salt was recrystallized and dried at 110°, at which temperature it showed constant weight.

The Purification and Dehydration of Solvents

Some of the alcohols, particularly *n*-propyl alcohol, were difficult to obtain pure, even when purchased from reliable sources. Acetone was purified by the bisulfite process.

A 90cm. side-drained, distillation column with 6 bulbs was used in fractionating the solvents; and most of the boiling points were determined by inserting through the center of the column a standardized thermometer, the entire length of which was surrounded by the vapors of the distilling liquid. This avoided stem corrections. The table of Young³² was used in

TABLE I
PHYSICAL CONSTANTS OF THE SOLVENTS

Solvent number	Solvent	B. p. range ° C.	Mean b. p. ° C.	Density 25°/4° corrected to a vacuum
1	Methyl alcohol	64.77–64.89	64.88	0.78705
2	Methyl alcohol	64.89–65.09	64.99	0.78735
3	Ethyl alcohol	78.29–78.31	78.30	0.78517
4	Ethyl alcohol	78.29–78.31	78.30	0.78515
5	<i>n</i> -Propyl alcohol	97.5–98.0	97.75	0.7989
6	<i>n</i> -Propyl alcohol	96.95–97.0	96.98	0.8026
7	<i>n</i> -Propyl alcohol	97.13–97.17	97.15	0.8009
8	<i>n</i> -Propyl alcohol	98.0–98.2	98.1	0.7993
9	<i>iso</i> Butyl alcohol	Standard thermometer not used	...	0.79807
10	<i>n</i> -Butyl alcohol	116.15–116.65	116.40	0.8059
11	Acetone	56.16–56.51	56.34	0.7852
12	Acetone		57.05	0.7864
13	Ethyl acetate	77.14–77.16	77.15	0.8945
14	Ethyl acetate	75.9–78.7	77.3	0.8923
15	Ether "over sodium" (im- ported)	Not determined	...	0.7081

³² Young, *J. Chem. Soc.*, **81**, 777 (1902).

correcting boiling points for changes in barometric pressure. The most reliable physical constants in the literature are probably those by Young³³ and Brunel, Crenshaw and Tobin.³⁴ From the data obtained later it is probable that slight amounts of organic impurities, especially those similar in nature to the solvent used, would have no appreciable effect on the solubility results, but even traces of water have a large influence. Accordingly, particular care was used in dehydrating the solvents. The alcohols were refluxed with metallic calcium, the ethyl ether and ethyl acetate with phosphorus pentoxide, and the acetone with powdered potassium hydroxide. The physical constants of the solvents are given in Table I on page 11.

The perchlorates, the solubilities of which were determined in each solvent, are given in Table II.

TABLE II
PERCHLORATES AND SOLVENTS USED

Solvent No.	
1	Rb, Na, K, Ba, Sr, Ca, Mg, Li.
2	(NH ₄), Cs.
3	Cs, Sr, Ba, Ca, Li.
4	Na, K, Rb, Mg, (NH ₄).
5	Rb, Sr, Mg, Ba, Ca, Li
6	Na.
7	K.
8	(NH ₄), Cs.
9	Rb, Cs, Na, K, Sr, Mg, Ba, Ca, (NH ₄), Li.
10	Rb, Cs, Na, K, Sr, Mg, Ba, Ca, (NH ₄), Li.
11	Rb, Cs, Na, K, Sr, Ba, Ca, (NH ₄), Li.
12	Ba.
13	Rb, Cs, Na, K, Sr, Mg, Ca, (NH ₄), Li.
14	Ba.
15	Rb, Cs, Na, K, Ba, Sr, Ca, (NH ₄), Li, Mg.

Apparatus and Methods

The usual procedure involved in the ordinary type of solubility determination could not be followed in this work. Most of the perchlorates dealt with were so extremely soluble in all the solvents used that sirupy solutions resulted. It was found that some equilibria between solute and solvent required that the solution be agitated for periods varying from 48 hours to more than 150 hours, and approaching the equilibrium from either side did not alter the circumstances. In many cases it required a week or more for the excess of solid to settle out so that a clear solution could be drawn off. In any case filtration was impracticable.

The temperature coefficient of solubility was often^o so high that it was almost impossible to estimate the requisite amount of the solute for a given volume of the solution. A solution a few degrees above 25° would often become so pasty upon cooling it to 25° that it would no longer flow.

³³ Young, *Proc. Dublin Phil. Soc.*, [2] **12**, 374 (1910).

³⁴ Brunel, Crenshaw and Tobin, *J. Am. Chem. Soc.*, **43**, 561 (1921).

These conditions demanded a thermostat constant to within 0.01° of the chosen temperature and capable of operation over long periods of time. A thermostat was made which satisfied these requirements in every way. The temperature, as indicated by a Beckmann thermometer, "set" by comparison with a thermometer certified by the Bureau of Standards, never varied more than 0.01° .

The method of procedure employed for making a solubility determination was as follows. The solution of the perchlorate was prepared by charging a dry 50cc. Erlenmeyer flask with sufficient anhydrous perchlorate to make 35–40 cc. of solution. The solvent was then added, and with the flask loosely stoppered, heat was applied, and solvent was evaporated until a saturated solution was obtained at a temperature near the boiling point of the solution. The flask was tightly stoppered and allowed to cool. Except when water or acetone was used as solvent, these solutions did not crystallize upon cooling to 0° or below, but often remained extremely viscous. Extreme cooling and long standing brought about crystallization, when scratching the inner walls of the flask in contact with the solution failed. Attempts to "seed out" these solutions always failed. When crystallization occurred, the amount of solvent necessary to all but dissolve the crystallized portion at 25° was added. A dry tube, about 18–20cc. capacity, was drawn down to prepare for sealing and charged with about a gram of the anhydrous salt. By means of a small glass funnel the tube was partly filled with the saturated solution and the crystallized portion obtained as described above. The solubility tube was then sealed and etched for identification.

The tubes thus prepared contained a solution saturated at a temperature slightly above the bath temperature and in contact both with the anhydrous salt and that crystallized from the solvent. They were rotated end-over-end in the thermostat usually for 24–48 hours, and then placed in a vertical position to allow the precipitate to settle.

After the solubility tubes had settled clear they were hastily withdrawn from the bath, dried, opened at the constricted upper extremity and samples were drawn off by means of a small pipet into weighed platinum crucibles contained in glass-stoppered weighing bottles. Samples for the solubility data were always taken from each of two or more solubility tubes of duplicate equilibria and the crucibles and containers were all weighed by use of a similar counterpoise. The vapor pressures of the solutions were, as a rule, very low because of extreme solubilities, but even when they were high the glass stoppers fitted so accurately that no loss of solvent occurred.

At the time samples were taken for solubility determination, a sample for density determination was transferred from 1 tube (or portions of 2 tubes) to a 10cc. or 25cc. pycnometer, the stopper of which was a capillary tube very accurately ground. The pycnometer and the pipets

used for sampling were stored in glass tubes immersed in the thermostat to attain the bath temperature. In case density determinations were carried out with portions of 2 solubility tubes, only those values were recorded which were obtained through the use of materials, analyses of which duplicated each other.

The platinum crucibles and containers were weighed, a few cubic centimeters of water added, and the crucibles placed upon an electric hot plate until the excess of solvent and water evaporated off. Repeating the treatment with water removed the solvent in all cases completely enough so that the weight of salt could, without danger of explosion, be determined by drying to constant weight at 250° in a current of air dried with phosphorus pentoxide. All solutions were analyzed by this procedure except those made with magnesium perchlorate, in which case, after evaporation of the solvent, enough sulfuric acid was added to convert all the magnesium perchlorate to magnesium sulfate, the solution evaporated to remove excess sulfuric acid and the magnesium sulfate ignited at 650° in an electric furnace. From its weight the perchlorate content of the solutions was calculated. In all cases the anhydrous perchlorates obtained were tested for chloride formed by possible decomposition. Any determination showing such a product was rejected.

Duplicate solubilities as high as 70–75% usually checked within $\pm 0.05\%$. In cases where low solubility demanded the use of large volumes, glass bulbs of 100 to 125cc. capacity were employed, and weight burets were used for sampling. Weighings were corrected to a vacuum, wherever such corrections were appreciable.

In all cases wherein a manipulation involved exclusion of atmospheric moisture, the operation was carried out in a large, glass-topped desiccator box, provided with a door for introduction of apparatus and materials, long-sleeved rubber gloves for arm manipulations, and into which a continuous stream of dry air was passed.

Few unusual phenomena were observed during the process of these solubility determinations. High temperature coefficients were observed to accompany high solubilities, and much heat was evolved during solution; in the case of acetone the solution often boiled. The temperature coefficient of the solution of strontium perchlorate in *isobutyl* alcohol is an enormous one, while in *n*-butyl alcohol it is not exceptional. In acetone solutions, no difficulty was encountered in crystallizing the salt from a saturated solution upon cooling.

The most unusual case of extreme solubility was that of anhydrous lithium perchlorate in anhydrous ether. The saturated solution at 25° contains 53.21% of lithium perchlorate and is extremely viscous. The solubility of lithium perchlorate trihydrate in absolute ether is, however, only 0.13%, and in ether saturated with water, 0.09%.

TABLE III
SOLUBILITIES OF PERCHLORATES

Solvent	Water	SODIUM PERCHLORATE							Ethyl acetate	Ethyl ether
		Methyl alcohol	Ethyl alcohol	n-Propyl alcohol	n-Butyl alcohol	isoButyl alcohol	Acetone			
Solv. dens.....		0.78705	0.78515	0.8026	0.8059	0.7981	0.7852	0.7881	0.8945	0.7081
Soln. dens.....	1.6821	1.0561	0.8685	0.8308	0.8167	0.8031	1.0732	0.9574	0.9574	0.7081
G./100 g. soln.....	67.70	33.93	12.82	4.66	1.83	0.78	34.10	8.80	8.80	insol.
G./100 cc. soln.....	113.88	35.833	11.134	3.871	1.495	0.6264	36.596	8.425	8.425	insol.
G./100 g. solv.....	209.60	51.355	14.705	4.888	1.864	0.786	51.745	9.649	9.649	insol.
G.m.w./100 cc. soln.....	0.9299	0.2926	0.0909	0.0316	0.0122	0.00515	0.2988	0.0719	0.0719	insol.
G.m.w./g.m.w. solv.....	0.3084	0.13435	0.0553	0.0240	0.0113	0.0048	0.2453	0.0694	0.0694	insol.
POTASSIUM PERCHLORATE										
Solv. dens.....		0.78705	0.78515	0.8009	0.8059	0.7981	0.7852	0.8945	0.8945	0.7081
Soln. dens.....	1.0096	0.7878	0.7852	0.8011	0.8060	0.7981	0.7868	0.8945	0.8945	0.7081
G./100 g. soln.....	2.02	0.105	0.012	0.010	0.0045	0.005	0.155	0.0015	0.0015	insol.
G./100 cc. soln.....	2.0394	0.0830	0.0094	0.0080	0.0036	0.0040	0.1179	0.0013	0.0013	insol.
G./100 g. solv.....	2.062	0.1051	0.012	0.010	0.0045	0.0050	0.1552	0.0015	0.0015	insol.
G.m.w./100 cc. soln.....	0.0145	0.00060	0.00070	0.00006	0.00003	0.00004	0.00085	0.00001	0.00001	insol.
G.m.w./g.m.w. solv.....	0.00268	0.00024	0.00004	0.00004	0.00024	0.00003	0.00065	0.00001	0.00001	insol.
RUBIDIUM PERCHLORATE										
Solv. dens.....		0.78705	0.78515	0.7989	0.8059	0.7981	0.7852	0.8945	0.8945	0.7081
Soln. dens.....	1.0060	0.7875	0.7851	0.7989	0.8059	0.7982	0.7865	0.8945	0.8945	0.7081
G./100 g. soln.....	1.32	0.060	0.009	0.006	0.002	0.004	0.095	0.0016	0.0016	insol.
G./100 cc. soln.....	1.328	0.0472	0.0071	0.0048	0.0016	0.0032	0.0745	0.0014	0.0014	insol.
G./100 g. solv.....	1.338	0.060	0.009	0.006	0.002	0.004	0.095	0.016	0.016	insol.
G.m.w./100 cc. soln.....	0.00718	0.00025	0.00004	0.00003	0.00001	0.00002	0.00040	0.00001	0.00001	insol.
G.m.w./g.m.w. solv.....	0.00130	0.00011	0.00002	0.00002	0.00001	0.00002	0.00030	0.00006	0.00006	insol.

TABLE III (Continued)

CESIUM PERCHLORATE									
Solvent	Water	Methyl alcohol	<i>n</i> -Propyl alcohol	<i>n</i> -Butyl alcohol	<i>iso</i> Butyl alcohol	Acetone	Ethyl acetate	Ethyl ether	
Solv. dens.....		0.78735	0.78517	0.7993	0.8059	0.7852	0.8945	0.7081	
Soln. dens.....	1.0165	0.7878	0.7852	0.7993	0.8059	0.7859	0.8945	0.7081	
G./100 g. soln.....	1.93	0.093	0.011	0.006	0.006	0.150	insol.	insol.	
G./100 cc. soln.....	1.961	0.0734	0.0086	0.0045	0.0048	0.1178	insol.	insol.	
G./100 g. solv.....	2.000	0.093	0.011	0.006	0.006	0.150	insol.	insol.	
G.m.w./100 cc. soln.....	0.00844	0.00032	0.00004	0.00002	0.00002	0.00051	insol.	insol.	
G.m.w./g.m.w. solv.....	0.00155	0.00013	0.00002	0.00002	0.00002	0.00057	insol.	insol.	
AMMONIUM PERCHLORATE									
Solv. dens.....		0.78735	0.78515	0.7993	0.8059	0.7852	0.8945	0.7081	
Soln. dens.....	1.0982	0.8218	0.79505	0.8016	0.8069	0.7997	0.8947	0.7081	
G./100 g. soln.....	19.95	6.41	1.872	0.385	0.017	2.21	0.032	insol.	
G./100 cc. soln.....	21.91	5.268	1.488	0.3086	0.0137	1.768	0.0286	insol.	
G./100 g. solv.....	24.922	6.862	1.907	0.3865	0.0170	2.260	0.032	insol.	
G.m.w./100 cc. soln.....	0.18647	0.04483	0.01266	0.00263	0.00012	0.01504	0.00024	insol.	
G.m.w./g.m.w. solv.....	0.03821	0.01871	0.00747	0.00198	0.00011	0.01117	0.00024	insol.	
BARIUM PERCHLORATE									
Solv. dens.....		0.78705	0.78517	0.7989	0.8059	0.7852	0.8923	0.7081	
Soln. dens.....	1.9403	1.7507	1.4157	1.2145	1.1342	1.4607	1.5236	0.7081	
G./100 g. soln.....	66.48	68.46	55.48	43.07	36.78	55.49	53.04	insol.	
G./100 cc. soln.....	128.99	119.85	78.543	52.309	41.716	81.054	80.812	insol.	
G./100 g. solv.....	198.33	217.06	124.62	75.654	58.168	124.67	112.95	insol.	
G.m.w./100 cc. soln.....	0.3836	0.3564	0.2336	0.15555	0.12405	0.2410	0.2403	insol.	
G.m.w./g.m.w. solv.....	0.10625	0.2068	0.1707	0.1352	0.1282	0.21525	0.29585	insol.	

TABLE III (Continued)

CALCIUM PERCHLORATE									
Solvent	Water	Methyl alcohol	n-Propyl alcohol	n-Butyl alcohol	isoButyl alcohol	Acetone	Ethyl acetate	Ethyl ether	
Solv. dens.....		0.78705	0.78517	0.7989	0.8059	0.7981	0.89457	0.7081	
Soln. dens.....	1.7191	1.6155	1.4342	1.3806	1.2868	1.0903	1.3325	0.7098	
G./100 g. soln.....	65.35	70.36	62.44	59.17	53.17	36.29	43.06	0.26	
G./100 cc. soln.....	112.34	113.68	89.551	81.690	68.419	39.567	57.377	0.1846	
G./100 g. solv.....	188.60	237.38	166.24	144.92	113.54	56.961	75.623	0.2607	
G.m.w./100 cc. soln.....	0.4701	0.4758	0.3747	0.3418	0.2863	0.1656	0.2401	0.0008	
G.m.w./g.m.w. solv.....	0.1422	0.3182	0.3204	0.3643	0.3520	0.1766	0.2787	0.0008	
STRONTIUM PERCHLORATE									
Solv. dens.....		0.78705	0.78517	0.7989	0.8059	0.7981	0.89457	0.7081	
Soln. dens.....	2.0837	1.6771	1.5539	1.4266	1.3394	1.2022	1.4717	0.7081	
G./100 g. soln.....	75.59	67.95	64.37	58.40	53.16	43.78	52.10	insol.	
G./100 cc. soln.....	157.51	113.95	100.01	83.31	71.205	52.63	89.92	insol.	
G./100 g. solv.....	309.67	212.01	180.66	140.38	113.49	77.87	136.93	insol.	
G.m.w./100 cc. soln.....	0.5497	0.3977	0.3491	0.2988	0.2485	0.1837	0.2676	insol.	
G.m.w./g.m.w. solv.....	0.1947	0.2371	0.2904	0.2943	0.2935	0.1633	0.4040	insol.	
MAGNESIUM PERCHLORATE									
Solv. dens.....		0.78705	0.78515	0.7989	0.8059	0.7981	0.89457	0.7081	
Soln. dens.....	1.4720	1.1057	0.9518	1.1926	1.1399	1.0609	1.3057	0.7101	
G./100 g. soln.....	49.90	34.14	19.33	42.33	39.16	31.27	41.49	0.29	
G./100 cc. soln.....	73.453	37.749	18.398	50.483	44.638	33.174	54.173	0.2059	
G./100 g. solv.....	99.601	51.838	23.962	73.400	64.366	45.497	70.911	0.2908	
G.m.w./100 cc. soln.....	0.3294	0.1691	0.3241	0.2261	0.2000	0.1486	0.2427	0.0009	
G.m.w./g.m.w. solv.....	0.0804	0.0744	0.0494	0.1975	0.21365	0.1510	0.2798	0.0010	

TABLE III (Concluded)

Solvent	Water	ANHYDROUS LITHIUM PERCHLORATE						Ethyl ether
		Methyl alcohol	Ethyl alcohol	n-Propyl alcohol	n-Butyl alcohol	isoButyl alcohol	Acetone	
Solv. dens.....		0.78705	0.78517	0.7989	0.8059	0.7981	0.7852	0.70817
Soln. dens.....	1.2683	1.3849	1.3173	1.2006	1.1326	1.0602	1.3233	1.2116
G./100 g. soln.....	37.385	64.57	60.28	51.22	44.23	36.73	57.72	53.21
G./100 cc. soln.....	47.42	89.44	79.41	61.49	49.25	38.94	76.38	64.47
G./100 g. solv.....	59.71	182.25	151.76	105.00	79.31	58.05	136.52	113.72
G.m.w./100 cc. soln.....	0.4457	0.8406	0.7463	0.5779	0.6646	0.3660	0.71785	0.6059
G.m.w./g.m.w. solv.....	0.1011	0.5487	0.6569	0.5929	0.5536	0.4043	0.7450	0.7920
LITHIUM PERCHLORATE TRIHYDRATE								
Solv. dens.....		0.78705	0.78517	0.7989	0.8059	0.7981	0.7852	0.70817
Soln. dens.....		1.1420	1.0241	0.9349	0.9082	0.8887	1.0965	0.7091
G./100 g. soln.....		60.95	42.16	26.82	21.40	18.85	49.04	0.196
G./100 cc. soln.....		69.61	43.18	25.07	19.435	16.75	53.77	0.139
G./100 g. solv.....		156.08	72.90	36.63	27.22	23.23	96.23	0.196
G.m.w./100 cc. soln.....		0.4338	0.2691	0.1563	0.1211	0.1044	0.3351	0.00086
G.m.w./g.m.w. solv.....		0.31165	0.20925	0.1372	0.1257	0.1073	0.3482	0.0905

The Solubility Table

The solubilities of the various perchlorates are recorded in the preceding table. The first 3 horizontal rows contain the actual experimental results, the remaining 4 were obtained by calculation from these.

The last row of figures, comprising the molal solubility per mole of solvent, constitutes the most interesting source of comparison. In general, considering especially the most soluble perchlorates and excluding ether, the molal solubilities in organic solvents are seen to be greater than those in water. The solubility of the perchlorates in the alcohols as a series is shown to decrease with increase in molecular weight of the solvent.

A point of interest is the greater molal solubility in *normal* as compared with *isobutyl* alcohol.

Ethyl acetate and acetone are seen to be equal in solvent action; this is hardly to be expected in view of their very different chemical properties. Acetone solutions crystallize more easily than those in ethyl acetate, show less viscosity and a much greater heat of solution.

All data in the preceding table refers to 25°.

THE PREPARATION AND PROPERTIES OF MAGNESIUM PERCHLORATE AND ITS USE AS A DRYING AGENT¹

Magnesium perchlorate was first prepared by Serrulas.¹ A more detailed study of this substance was made by Weinland and Ensgraber,⁶ who prepared the hydrate, $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, by drying the sample in a vacuum over phosphorus pentoxide. They failed to note that this treatment yields finally the lower hydrate, $\text{Mg}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$, because the dehydration is rather slow even in its early stages. No mention of this second hydrate was found in the literature.

Preparation of Magnesium Perchlorate Hexahydrate

The purest imported magnesium oxide was treated with a slight excess of pure dil. perchloric acid, which was prepared by the method of Willard.³⁰ The solution thus formed was evaporated until crystallization began at the surface and fumes of perchloric acid were being given off. The mixture was then allowed to cool to room temperature with the addition of sufficient water to keep the crystal mass semifluid. After centrifugal drainage the product, containing but a slight amount of perchloric acid, was redissolved, recrystallized, and again centrifuged. The needle-like crystals thus obtained were shown by spectroscopic examination to contain no calcium or barium in spite of the fact that the oxide employed in their preparation was similarly shown to contain traces of these impurities.

Analysis of the Hexahydrate for Water of Crystallization

The salt prepared as above described could not be freed from its slight excess of water by drying at 110° , since after 24 hours of such treatment a sample lost 30% of its crystal water. A few grams of the material was dried by storing for 4 weeks over anhydrous magnesium perchlorate in a desiccator at room temperature.

A weighed portion of the material in a platinum crucible was dissolved in water and a slight excess of sulfuric acid added. The solution was then evaporated and heated until the excess of the sulfuric acid was evaporated, using a ring burner, and the last traces were removed by igniting the crucible for 10 minutes in an electric crucible furnace at 650° . From the weight of the magnesium sulfate the weight of magnesium perchlorate was calculated and the weight of crystal water lost in the process thus obtained. The mean of two closely agreeing duplicates gave 32.76% water of crystallization while the theoretical value for the hexahydrate is 32.62%. The remainder of the material when analyzed after being kept for 3 months longer over anhydrous magnesium perchlorate, gave by a single determination 32.40% of water of crystallization; this leads

to the conclusion that the hexahydrate of magnesium perchlorate is not further dehydrated in contact with the anhydrous reagent.

The hexahydrate thus obtained melted between 145° and 147° and its density as determined by immersion in carbon tetrachloride, in which it is insoluble, was found to be 1.970 at $25^{\circ}/4^{\circ}$, corrected to a vacuum. In this determination the usual precautions were observed, such as pulverizing the sample and evacuating after immersion, to remove trapped air. Although this salt as crystallized from water solutions does not deliquesce in air, the fused material does so in a pronounced manner.

Preparation and Analysis of Magnesium Perchlorate Trihydrate

About 50 g. of the hexahydrate, as above described, was stored in an efficient vacuum desiccator over a generous portion of phosphorus pentoxide, changed at frequent intervals, and the desiccator was frequently pumped out so that a high vacuum was maintained continuously. When the temperature was kept at 0° or less, no loss of crystal water on the part of the hexahydrate was apparent, the weight of a sample remaining constant. When the temperature was allowed to rise to 20 – 25° , other conditions being equal, the salt began slowly to give up a part of its crystal water. The drying was continued during 4 months and the salt was analyzed at intervals of 1 month by the method previously described, with the following results: the original water content was 32.6% (hexahydrate); after 1 month it was reduced to 24.0%; after 2 months, 22.0%; after 3 months, 20.5%; and after 4 months, 19.75%. The percentage of water calculated for the trihydrate formula is 19.50. Thus the total water removed during these intervals of time was approximately 66.0%, 15.5%, 11.5% and 6.0%, respectively. The graph of the percentage of water removed plotted against the time interval involved showed the curve to be asymptotic to the time axis, and it became apparent that after sufficient time the theoretical value for the trihydrate would eventually have been reached. Further treatment was not given, however, and the properties of the material thus obtained were studied.

When either the trihydrate or the hexahydrate was completely melted and allowed to cool slowly, it solidified at 145 – 147° . Perhaps this is the eutectic point of these 2 hydrates. The density of the trihydrate was found by displacement of carbon tetrachloride to be 2.044 at $25^{\circ}/4^{\circ}$, corrected to a vacuum.

Preparation of Anhydrous Magnesium Perchlorate

Portions of about 100 g. of the hexahydrate, prepared as already described, were heated in large porcelain crucibles to a temperature slightly above the melting point. The crucibles were supported on trays contained within a Pyrex tube 8 cm. in diameter and 90 cm. long. The tube was electrically heated and a stream of air dried by phosphorus pentoxide

passed through the tube continuously. A temperature of 170° served to drive off the greater portion of the crystal water, but at the end of the process the temperature was raised to 250° . The fused material, as it loses water, becomes heavily encrusted and must be stirred at frequent intervals. At the end the mass became pasty, and finally when all the water was removed a dry, white material remained which was taken from the crucibles while still hot and ground to a powder. It was then returned to the drying train, kept at $230\text{--}250^{\circ}$ and samples were taken while hot to insure absence of moisture.

Water solutions of magnesium perchlorate so prepared were neutral and free from chloride. It was thus shown that anhydrous magnesium perchlorate is completely stable at 250° . At a slightly higher temperature slow decomposition begins, oxide and chloride being formed.

When anhydrous magnesium perchlorate was gradually elevated in temperature from 250° to about 400° it decomposed quietly without fusing, leaving a residue consisting principally of magnesium oxide. In this way the residual moisture in the salt was determined. Weighed portions of the salt were completely decomposed at 400° and the moisture evolved with the gas was absorbed in a phosphorus pentoxide tube. A blank correction was applied and the air was carefully purified. The samples were taken hot to avoid absorption of atmospheric moisture and glass stoppered sampling tubes were used for weighing. By this direct measurement the moisture found was less than 0.1% . In view of the extreme affinity of anhydrous magnesium perchlorate for water, even this value may not be as low as that in the original material prior to sampling.

Anhydrous magnesium perchlorate has a density of 2.60 at $25^{\circ}/4^{\circ}$ corrected to a vacuum as determined by displacement of carbon tetrachloride in the manner already described. When water is added to it a hissing sound is produced very similar to that produced by the addition of water to phosphorus pentoxide.

The Efficiency of Anhydrous Magnesium Perchlorate as a Drying Agent

Two ground glass-stoppered U-tubes were filled with phosphorus pentoxide and asbestos in alternate layers, one tube being used as a counterpoise. A third U-tube of identical proportions was filled with anhydrous magnesium perchlorate and cotton wool in alternate layers. The weight of magnesium perchlorate in the tube was 9.06 g. The total length of the column of drying agent in each tube was about 13 cm. All weighings were made by counterpoise. The tubes were always allowed to stand in the balance case for a considerable length of time in order to insure equilibrium conditions and the stopcocks were always opened for a moment just before a weighing. The train of apparatus and air flow was as follows. Air under pressure was passed through a calibrated flow-meter

and then saturated with moisture by passing through a potash bulb containing water. From the potash bulb saturator the air passed successively through the magnesium perchlorate tube, the phosphorus pentoxide tube and finally a protection tube filled with phosphorus pentoxide to prevent backward diffusion of moisture. Small plugs of cotton wool were placed between all connections to prevent passage of spray or dust particles from one unit to another. All weighed parts of the train as well as the saturator bulb were immersed up to the horizontal cross connections in a thermostat accurately maintained at 25°.

The rate of flow of the moist air was varied from 1.5 to 3.5 liters per hour. The magnesium perchlorate and phosphorus pentoxide tubes were weighed 14 times during more than 8 hours of continuous test. At no time during the test had a weighable amount of water vapor escaped absorption in the magnesium perchlorate tube. Thus, after the 9.06 g. of magnesium perchlorate had taken up 5.23 g. of water the phosphorus pentoxide tube directly following weighed exactly the same as it did before the experiment. At the completion of the test about 1 g. of magnesium perchlorate was still unchanged. It was thus found that the magnesium perchlorate had absorbed nearly 60% of its own weight of moisture while the residual water vapor in over 210 liters of air used in the experiment was unweighable.

With the 10cm. U-tubes described above, the maximum rate of flow which would insure complete removal of water from air saturated at 25° was found to be 5.0 liters per hour. Thus with columns of equal length the rate of absorption is seen to be quite limited in comparison with that of phosphorus pentoxide. This is to be expected, since the mechanism of the absorption in the case of phosphorus pentoxide is that of true chemical combination rather than formation of water of crystallization, as in the case of magnesium perchlorate.

Efficiency of the Trihydrate as a Dehydrating Agent

The fact that phosphorus pentoxide was found to be incapable at a temperature of 0° and less, of drying magnesium perchlorate below the hexahydrate stage, while at ordinary temperatures the trihydrate was thus formed indicated that this salt also possessed great dehydrating power. Accordingly, experiments were run duplicating conditions as above described for anhydrous magnesium perchlorate, the rate of flow and the temperature of the absorbent being varied. The results of these determinations are given in the following table.

°	Temperature ° C.	Rate of gas flow L./hr.	H ₂ O unabsorbed by Mg(ClO ₄) ₂ ·3H ₂ O G.	Duration of experiment Hrs.
	0	5.2	0.0000	11
	25	5.0	0.0049	17
	0	10.0	0.0024	2

At 0° and at rates of flow up to 5 liters per hour the trihydrate is as effective as phosphorus pentoxide and anhydrous magnesium perchlorate. At rates of flow up to 10 liters per hour the efficiency, while still high, falls off rapidly.

Among the advantages possessed by magnesium perchlorate as a drying agent in comparison with phosphorus pentoxide are the following.

1. The weight of water absorbed per unit weight of desiccating agent is several times greater with anhydrous magnesium perchlorate than with phosphorus pentoxide.
2. Anhydrous magnesium perchlorate does not become sticky upon handling, does not form channels through use and contracts in volume upon absorbing moisture.
3. It can be recovered and reactivated repeatedly.
4. Being a neutral drying agent it offers many possibilities as a dehydrating agent for materials for which phosphorus pentoxide and conc. sulfuric acid are not permissible. Work upon this phase of the subject will be taken up at a future date.

THE SEPARATION AND DETERMINATION OF SODIUM AND LITHIUM BY PRECIPITATION FROM ALCOHOLIC PERCHLORATE SOLUTION¹

A review of the literature on the separation of sodium and lithium shows that none of the methods so far suggested is entirely satisfactory. The solubility corrections are usually large and the separation must be repeated one or more times.

Most of the methods proposed involve the extraction of lithium chloride from the anhydrous mixed chlorides of the metals involved, using an organic solvent or mixture of solvents in which the chlorides other than lithium chloride are insoluble. Another general type of procedure consists in dissolving the mixed chlorides in the least quantity of water necessary for their solution, followed by the precipitation of the chlorides other than lithium chloride, by the addition of an organic solvent or mixture of solvents in which the chlorides precipitated are but slightly soluble, a correction being applied for this slight solubility.

A full and critical discussion of the papers relating to this subject up to the year 1912 is given by Skinner and Collins.³⁵ Of the more recent work, that of Winkler³⁶ employs *isobutyl* alcohol in an extraction method, more than one extraction being required in each analysis. The method is tedious in operation and subject to errors because of the number of manipulations involved. In the method of Palkin³⁷ a concentrated aqueous solution of the mixed chlorides is precipitated by the addition of anhydrous alcohol followed by ether. The chlorides thus precipitated are filtered, and the small amount remaining in solution is recovered by evaporating to dryness and extracting with alcohol and ether. The method is an improvement over the others since it eliminates the solubility correction, but the use of the volatile ether is a disadvantage.

The methods in which chlorides are precipitated rather than extracted most closely approximate the usual analytical processes and are theoretically more accurate. However, Palkin's process is strictly speaking not really such, as the precipitant does not carry a component which enters into the composition of the precipitate formed; moreover, the method is applied to saturated rather than dilute solutions.

The object of the present section is the development of a method for the separation and determination of lithium and sodium, based upon precipitation of the material separated, in a manner analogous to the usual analytical practice.

³⁵ Skinner and Collins, U. S. Dept. Agr. *Bur. Chem. Bull.* **153** (1912).

³⁶ Winkler, *Z. and Chem.*, **52**, 628 (1913).

³⁷ Palkin, *J. Am. Chem. Soc.*, **38**, (1916).

The Method

The process, in brief, consists in the precipitation and separation of sodium chloride from a solution of the mixed perchlorates of sodium and lithium in *n*-butyl alcohol by the addition of a butyl alcohol solution of hydrogen chloride according to the reaction, $\text{NaClO}_4 + \text{HCl} = \text{NaCl} + \text{HClO}_4$. The reagent is added to the solution of the perchlorates until a 6% acid concentration is attained. The precipitated sodium chloride is filtered on a weighed Gooch crucible, washed with a 6–7% solution of hydrogen chloride in butyl alcohol, dried at 250° and ignited for a few minutes at 600°. The lithium chloride, after removal of the organic matter by evaporation, is determined by conversion to lithium sulfate, a correction being applied for the almost negligible amount of sodium chloride remaining in the filtrate. In some cases the reagents give a slight blank. Potassium cannot be present since its perchlorate is insoluble in alcohol.

Preparation of Materials

Normal Butyl Alcohol.—This material is readily obtainable on the market at the present time at a moderate price. The alcohol used in this research had a boiling range of 112–118° and a density of 0.8065 at 25°/4°; 60% of this product boiled within a range of 1° of the true boiling point. This fraction, when dried by refluxing with a slight excess of metallic calcium, had a boiling range of 116.2–116.7° and a density of 0.8060 at 25°/4°. Half of this fraction boiled within a range of 0.05°. In most of the work the 60% fraction, obtained as described above, was used. Experiments were also carried out using alcohol of widely different constants, the data concerning which will be recorded later.

Perchloric Acid.—The method of Willard³⁰ was used for the preparation of the perchloric acid. It was twice distilled under a pressure of from 5 to 15 mm. and contained about 72% HClO_4 . Ten g. of this material when evaporated in a platinum crucible gave an almost unweighable residue after ignition.

Sodium Chloride.—An imported product of highest purity was used.

Sodium Perchlorate.—This material was prepared by treatment of the purest sodium carbonate with a slight excess of dil. perchloric acid. The anhydrous sodium perchlorate was obtained by crystallization above 50°, using centrifugal drainage. The product thus obtained was dried in a current of dry air at a temperature of 250°. To obtain samples of sodium perchlorate for the analytical separations, pure sodium chloride in weighed portions was evaporated on a hot plate with a slight excess of perchloric acid until fumes of perchloric acid were no longer evolved.

Lithium Chloride.—This material was prepared from a product which contained some sodium chloride. It was freed from the latter by solution in hot butyl alcohol under a reflux condenser. The solution was cooled and the sodium chloride filtered off. The lithium chloride in the filtrate was recovered by evaporation in a platinum dish to a pasty mass which was dried in an electric oven at 100°. It was further heated in a muffle at 500° and finally fused in a current of hydrogen chloride dried with sulfuric acid. The product thus obtained was cooled, crushed, and powdered under conditions which insured no contact with atmospheric moisture. It was used only in the solubility determinations.

Lithium Perchlorate.—The method employed in the preparation of this material was that described by Richards and Willard.⁹ Lithium nitrate was purified by recrystallization and then precipitated by the addition of hydrofluoric acid. The lithium fluoride

was converted to perchlorate by evaporation with pure perchloric acid. This was then recrystallized from water with centrifugal drainage, platinum vessels being used throughout. The lithium perchlorate trihydrate thus obtained was dehydrated by fusion in a current of dry air at 250°.

Samples of this anhydrous lithium perchlorate were weighed into platinum crucibles contained in glass-stoppered weighing bottles and again fused by placing the crucibles in a drying tube at 250°, through which passed a current of dry air. The crucibles and contents were then replaced in their weighing bottles, cooled, and reweighed. The original weight was usually lowered a fraction of a milligram due to the very slight hygroscopic nature of anhydrous lithium perchlorate.

The Solution of Hydrogen Chloride in Butyl Alcohol.—Butyl alcohol was treated with hydrogen chloride generated in the usual way by the action of conc. sulfuric acid on sodium chloride or conc. hydrochloric acid; 200 cc. of 20% solution could be prepared in 2 or 3 hours. For testing the strength of these solutions an hydrometer serves admirably. For use in this connection a density-concentration curve was constructed between the limits of 0 and 20% hydrogen chloride. It was found to be sufficiently close to a straight line function so that values between those given in the following table could be obtained by interpolation.

TABLE I

DENSITY OF SOLUTIONS OF HYDROGEN CHLORIDE IN DRY NORMAL BUTYL ALCOHOL							
HCl %	Density	HCl %	Density	HCl %	Density	HCl %	Density
0	0.8060	6	0.8425	11	0.8685	16	0.8895
1	0.8130	7	0.8485	12	0.8730	17	0.8935
2	0.8195	8	0.8540	13	0.8770	18	0.8960
3	0.8255	9	0.8590	14	0.8810	19	0.9010
4	0.8315	10	0.8635	15	0.8855	20	0.9050
5	0.8370						

These values were obtained by using a pycnometer and thermostat and refer to 25°/4° corrected to vacuum. The hydrochloric acid was determined by titration with standard alkali.

Conditions Affecting the Precipitation of Sodium Chloride from a Solution of Sodium Perchlorate in Butyl Alcohol

Several factors, some unexpected, were found to influence the quantitative separation of sodium and lithium from solution in anhydrous butyl alcohol by the addition of the solution of hydrogen chloride in butyl alcohol. The factors in the order of their importance are: (1) temperature of precipitation; (2) concentration of hydrochloric acid, giving minimum solubility of sodium chloride; (3) conditions favoring ease of filtration; (4) prerequisites for drying and ignition of the sodium chloride obtained; (5) physical constants of butyl alcohol used in the method; (6) treatment of filtrates from sodium chloride for recovery of lithium. These factors will be taken up in the order given.

Temperature of Precipitation.—Sodium chloride precipitated from boiling solutions of sodium perchlorate in butyl alcohol when filtered on asbestos, washed, and dried at 250° for a long time, is perfectly white, but upon ignition to 500–600° it becomes dark gray and when then dis-

solved in water a black deposit of carbon is obtained. This results from occlusion of solvent in the precipitated sodium chloride. The error in weight of the precipitated sodium chloride, due to this cause, is variable and too large to be neglected. Precipitation at room temperature gave a similar result but much less carbon was obtained. Wash solutions such as acetone, ether and carbon tetrachloride, are incapable of removing the occluded solvent from the precipitate. Ignition of the sodium chloride containing carbon in a stream of oxygen did not remove the impurity. The lower the temperature of the solution from which sodium chloride is precipitated, the less the tendency it shows to occlude solvent. When precipitated at -15° to -20° the dried and ignited salt contains no carbon but is pure sodium chloride.

Effect of Acid Concentration Upon the Solubility of Sodium Chloride.—Solutions of sodium perchlorate of known content were precipitated by the addition of butyl alcohol containing 20% of hydrogen chloride. A definite excess of hydrogen chloride was then added over that required for precipitation. After being heated to boiling, the precipitated samples were cooled to room temperature, filtered through asbestos, and washed with solutions of hydrogen chloride in butyl alcohol of the same strength as those from which the sodium chloride was precipitated. The pre-

TABLE II
SOLUBILITIES IN ANHYDROUS NORMAL BUTYL ALCOHOL AT 25°

G. per 100 g. solution			G. per 100 g. solution		
		Density $25^{\circ}/4^{\circ}$			Density $25^{\circ}/4^{\circ}$
LiClO ₄	44.23	1.1341	LiCl.....	11.49	0.8713
NaClO ₄	1.83	0.8167	NaCl.....	0.014 ^a	0.8060

^a 0.0116 g. per 100 cc.

TABLE III
SOLUBILITY OF SODIUM CHLORIDE PRECIPITATED FROM ANHYDROUS BUTYL ALCOHOL
CONTAINING 6% OF HYDROGEN CHLORIDE

	NaCl taken	NaCl found	Vol. fil- trate and washings ^a	Free HClO ₄ present	LiClO ₄ present	Solubility of NaCl in 100 cc.
	G.	G.	Cc.	%	G.	G.
1	0.3021	0.3007	102	...		0.0014
2	0.3004	0.2989	110	...	0.1720	0.0014
3	0.3031	0.3020	102	...		0.0011
4	0.3510	0.3493	87	...	0.0356	0.0019
5	0.1549	0.1546	52	0.5		0.0006
6	0.1593	0.1590	55	0.5		0.0006
7 ^b	0.1034	0.1027	43	0.5		0.0016
8	0.3505	0.3481	98	1.5		0.0024

^a Consisting of butyl alcohol containing hydrogen chloride and a little perchloric acid.

^b Alcohol as received, not dried or distilled.

precipitate was dried at 250° , ignited at $500\text{--}600^{\circ}$ and the sodium chloride found, corrected for its carbon content, was compared with the amount present. The concentration of hydrogen chloride was gradually increased, until at 6% to 7% the solubility of sodium chloride reached a minimum of 0.6 mg. per 100 cc. This excess of hydrogen chloride can be obtained closely enough by adding to the solution of the perchlorate half as many cc. of 20% solution of hydrogen chloride in butyl alcohol, as there are grams of the solution. The wash solution is made in the same way.

The solubilities of the various salts involved are shown in the preceding tables.

It is evident from the above data that the solubility of sodium chloride is greatly reduced by the presence of hydrogen chloride. That of lithium chloride, is, however, much less affected. The addition of 4.9% of hydrogen chloride reduced it from 11.49 g. to 9.60 g. per 100 g. of solution. No lithium chloride was precipitated when a 20% solution of hydrogen chloride in butyl alcohol was added to a 40% solution of lithium perchlorate in the same solvent. The solubility of sodium chloride is reduced from 11.6 mg. per 100 cc. in pure, dry butyl alcohol to 1.4 mg. by the addition of 6% hydrogen chloride and to 0.6 mg. per 100 cc. by the further addition of 0.5% of 70% perchloric acid. The reason for this latter decrease is not evident. More than 0.5% of perchloric acid increases the solubility. In unpurified and undried 6% hydrogen chloride—alcohol containing 0.5% of perchloric acid, the solubility rises to 1.6 mg. per 100 cc.

Conditions Favoring Filtration.—The higher the temperature of precipitation, the greater the ease of filtration. From a boiling sodium perchlorate solution in butyl alcohol, the sodium chloride precipitated is coarse, settles rapidly, and filters easily. From the same solution precipitated at room temperature, the precipitate is more gelatinous, settles slowly, and is difficult to filter and wash. The same solution precipitated at -15° to -20° cannot be filtered.

Since it is desirable to utilize cold precipitation to prevent occlusion of solvent by the sodium chloride, solutions precipitated at -15° to -20° were heated to boiling and allowed to cool to room temperature before filtration. The precipitate of sodium chloride should be formed by adding, drop by drop, to the cold solution, 1–1.5 cc. of the hydrogen chloride—butyl alcohol reagent, the remainder to form a 6% acid—butyl alcohol solution being added rapidly. Under these conditions the precipitated sodium chloride, after boiling, settles rapidly, and after cooling to room temperature can be filtered clear, using a Gooch crucible. It is washed with a 6–7% solution of acid in butyl alcohol. If the concentration of acid is over 6%, coagulation of the sodium chloride is less effective.

Physical Constants of the Butyl Alcohol Used in the Method.—In view of the results obtained by Winkler³⁶ in the use of *isobutyl* alcohol,

a rather carefully purified *n*-butyl alcohol was employed in most of the work recorded in this paper. Winkler used *isobutyl* alcohol dehydrated over caustic potash and which had a boiling range of one degree, 106–107°. It was further specified that this fraction of the dried sample was necessary for good results. It will be shown later that drying only and no fractionation is required.

Treatment of Filtrates from Sodium Chloride for Recovery of Lithium.

—The filtrates from the sodium chloride precipitate consisted of a butyl alcohol solution of hydrogen chloride and perchloric acid, lithium and a slight amount of sodium as perchlorate or chloride, the latter resulting from the almost negligible solubility of sodium chloride. The salts were recovered by evaporation of the solvent and volatile acids, converted to lithium and sodium sulfates, ignited and weighed. From this weight, corrected for the known amount of sodium sulfate, the amount of lithium was calculated.

Although the dilute solution of anhydrous perchloric acid and lithium perchlorate could be boiled without trouble, evaporation to dryness without first adding water resulted in a violent deflagration; 30 to 50 cc. of water was added to 50–100 cc. of the cold alcoholic solution and 2 immiscible layers were obtained. The under layer of water extracted most, if not all, of the products of solution from the upper alcoholic layer. When this mixture was evaporated on a steam-bath the alcoholic layer evaporated completely, leaving the greater part of the water solution of lithium and sodium perchlorates and perchloric acid. The organic matter remaining was eventually oxidized, and after the addition of sulfuric acid the evaporation was continued to dryness. The lithium sulfate was then dissolved in a little water, washed into a weighed platinum crucible, covered and heated over a ring burner to remove excess of sulfuric acid. The conversion of lithium perchlorate to lithium sulfate is more easily carried out without loss than conversion of lithium chloride to sulfate. The lithium sulfate was ignited in a muffle at 600° for 5 to 10 minutes, or to constant weight in case of large amounts. Samples thus treated were neutral and could be fused without loss in weight.

Separation of Sodium and Lithium

When free from potassium, the mixed chlorides (free from sulfate) obtained by the J. Lawrence Smith or other method, are evaporated to dryness with excess of perchloric acid. A second evaporation is desirable if the amount is large. If potassium is present it is first separated by the usual perchlorate method and the filtrate, *after addition of water*, to avoid explosion, is evaporated to dryness. Since a definite amount of perchloric acid should be present, it is desirable to remove first all excess of acid.

The mixed perchlorates of sodium and lithium free from perchloric acid are dissolved in anhydrous *n*-butyl alcohol using at least 15 g. or 18.5 cc. for each 100 mg. of sodium chloride present. The containing beakers may be conveniently weighed upon a small platform balance. The mixture dissolves readily if the alcohol is heated to boiling, which can be done with a burner over a wire gauze; 0.1 cc. of 70% perchloric acid is added and the solution is cooled to -15° by means of a freezing mixture. The sodium chloride is precipitated by adding from a buret, drop by drop, with constant stirring, 1–1.5 cc. of a 20% solution of hydrogen chloride in anhydrous butyl alcohol after which the amount necessary to form a 6% solution is rapidly added (half as many cubic centimeters as there are grams in the solution to be precipitated). The precipitate of sodium chloride is then coagulated by heating the solution to boiling on a wire gauze with a free flame. After cooling to room temperature the sodium chloride is filtered on a weighed Gooch crucible and washed 8 or 10 times with a 6–7% solution of hydrogen chloride in butyl alcohol. (A rubber-tipped rod can be used in transferring the precipitate from beaker to crucible. It is well to preserve it by washing with a little acetone after use.) The sodium chloride is dried for one hour at 250° and ignited for 5 to 8 minutes at 600° in a muffle furnace (a free flame may be used but a very dull red must not be exceeded). A correction of 0.6 mg. for the sodium chloride remaining in each 100 cc. of filtrate and washings is added to the weight of sodium chloride found, to obtain the total sodium chloride present.

The filtrate and washings from the sodium chloride are diluted with $\frac{1}{3}$ their volume of water, (to avoid subsequent deflagration) forming 2 layers, and the whole is evaporated on the steam-bath in such a way as to avoid any condensation on the upper part of the beaker, which causes loss by "creeping." It is well to add 5 to 10 cc. of water at the end to make the removal of organic matter more complete before the perchloric acid takes effect. By such treatment a colorless residue of lithium perchlorate and perchloric acid can be obtained. If a slight brown coloration is present, remove the watch glass supports from the beaker and heat the covered beaker on a wire gauze to fumes of perchloric acid. If any brown color remains adhering to the beaker walls after this treatment, it can be removed by brushing the walls of the beaker with the flame. If not enough perchloric acid is present to oxidize the last traces of organic matter, a few drops are to be added. When the brown coloration is removed, 0.5 cc. of conc. sulfuric acid is added, the watch glass replaced and the acid fumed off, using either a hot plate or low flame and wire gauze. The beaker is then cooled, 5 to 10 cc. of water is added, and the cover glass and beaker walls washed. The lithium sulfate is then transferred to a platinum crucible previously ignited and weighed with its lid. The solution is cautiously evaporated to dryness and the covered crucible is heated, preferably by a ring burner, until every trace of acid is removed, after which it is heated to 600° in a muffle for 5 to 10 minutes. When the same treatment is carried out using a free flame and a very dull red heat, some reduction to sulfide often takes place, due to diffusion of the flame gases through the platinum. Fusing with a free flame to check the weight obtained by the above treatment is possible if the temperature is not too high or the treatment too long.

The weight of lithium sulfate is to be corrected for its sodium sulfate content by subtracting the weight of the solubility correction calculated as sodium sulfate, or 0.7 mg. per 100 cc. of filtrate and washings. A further correction to be applied is a blank for the reagents employed. This correction is found by precipitating a weighed sample of sodium chloride in the manner above described. One cc. of perchloric acid is ample for any ordinary quantity of salts to be converted and the subsequent additions of 0.5 cc. each of sulfuric acid and perchloric acid are enough to provide excess. The weight of material obtained at the end of this process should be less than 1 mg. when corrected for the sodium chloride solubility.

Gooch crucibles with 0.5mm. holes are much better than those with large holes. Platinum Gooch crucibles with their much smaller perforations are still better. A heavy mat of asbestos is essential and a perforated porcelain disk should be placed on it to prevent disturbance of the mat. If platinum-sponge filtering crucibles are used, weighing of the empty crucible should be made after the sodium chloride has been washed out with water, since spongy platinum is slightly attacked. Asbestos for use in filtrations with solutions of hydrogen chloride in butyl alcohol should be refluxed with some of this material in preparation for its use. The same crucible should be used many times over, and in such a case previous treatment of the asbestos with the acid-alcohol solution is not necessary. To show the effect of the solvent upon asbestos, the same crucible was used repeatedly, starting with untreated asbestos. The sodium chloride was washed out each time. The following successive weights were obtained: 26.6413, 26.6405, 26.6401, 26.6401, 26.6401. In order to avoid an additional operation the filtration with suction can be made directly from the crucible to a beaker by using a vacuum desiccator of the usual form but with a hole provided in the cover for the passage of a filtering tube and rubber stopper. In this way the beaker to receive the filtrate can be placed in the bottom of the desiccator. The filtering tube should have a small perforation in its side about an inch from the bottom to prevent spattering.

The filtrates were rapidly evaporated on the steam-bath by immersing the beaker in a copper capsule flanged at the top and fitted to the rings of the steam-bath so that condensation did not take place on the walls of the beaker or cover glass. This is very important because the alcoholic solution shows a strong tendency to "creep."

The value of the method was tested by a series of analyses of known mixtures, with the results recorded in the following table.

TABLE IV
SEPARATION AND ESTIMATION OF SODIUM AND LITHIUM

Expt.	NaCl taken G.	NaCl found G.	Error G.	LiClO ₄ taken G.	LiCl calc. G.	Li ₂ SO ₄ found G.	LiCl found G.	Error G.
1	0.1521	0.1519	-0.0002	0.4819	0.1920	0.2488	0.1919	-0.0001
2	0.1481	0.1478	-0.0003					
3	0.1017	0.1017	0.0000	0.5534	0.2205	0.2860	0.2206	+0.0001
4	0.2027	0.2024	-0.0003	0.5295	0.2110	0.2736	0.2110	0.0000
5	0.1016	0.1016	0.0000	0.3004	0.1197	0.1558	0.1202	+0.0005
6	0.0217	0.0218	+0.0001	0.4455	0.1775	0.2315	0.1785	+0.0010
7	0.0502	0.0503	+0.0001	1.5354	0.6118	0.7929	0.6116	-0.0002
8 ^a	0.1017	0.1019	+0.0002					

^a Alcohol dried but not fractionated; boiling range 112-118°.

The separation of sodium from very large amounts of lithium is accomplished by one precipitation (Expt. 7).

In case it is desired to avoid a cold precipitation, (a step which requires but one short additional operation), the method can be applied exactly as described, omitting cooling to -15° before precipitation, and adding the precipitant to the mixed perchlorate solution at nearly its boiling temperature. In this case the solubility of sodium chloride was found to be 1.6 mg. in 100 cc. of solvent. The carbon occluded by a precipitate of about 0.5 g. of sodium chloride is approximately 1.5-1.0 mg. under these conditions. The weight of sodium chloride in the precipitate can

be determined by dissolving it in water, drying the crucible with its carbon impurity, and weighing after filtration rather than before.

Suggested Perchlorate Methods for New Quantitative Separations*

The well known perchlorate method for separating sodium and potassium has been improved at frequent intervals. The use of ethyl acetate as solvent rather than anhydrous ethyl alcohol has been suggested, the former being more readily obtained. Accordingly the solubility data concerned were determined in connection with this paper.

By reference to the tables previously given the solubility of sodium perchlorate in pure ethyl acetate is seen to be 8.80% at 25°/4°, the solution having a density of 0.9574 at 25°/4°. The corresponding solubility in ethyl alcohol is 12.82%. Sodium perchlorate dissolves in ethyl acetate containing 0.2% perchloric acid added in the form of the 70% acid, to the extent of 9.25% giving a solution density of 0.9622 at 25°/4° compared with 0.0869 at 25°/4° for the original 0.2% perchloric acid solution.

The solubility of potassium perchlorate in pure ethyl acetate is 1.3 mg. per 100 cc. and in ethyl alcohol 9.4 mg. per 100 cc. while in ethyl acetate containing 0.2% perchloric acid the solubility increases to 1.6 mg. per 100 cc. It is evident therefore that while the substitution of ethyl acetate for alcohol decreases the solubility of the sodium salt very little, it decreases that of the potassium salt enormously.

The idea of developing a perchlorate method for the separation of strontium and calcium as well as calcium and magnesium was also tested in a preliminary manner in connection with this paper. Since it has been shown above that sodium may be quantitatively precipitated as chloride and separated from lithium by adding a solution of hydrochloric acid in normal butyl alcohol to the alcoholic solution of the mixed perchlorates, it was sought to separate strontium and calcium using nitric acid as the precipitant. Upon testing several solvents normal butyl alcohol was found to be suitable while the lower alcohols are progressively less suited. Strontium nitrate dissolves in pure normal butyl alcohol to the extent of 6.5 mg. per 100 cc. at 25° C. The solubility of strontium nitrate in butyl alcohol containing 5% by weight of 90% nitric acid is practically nothing. A solution of strontium perchlorate in butyl alcohol can be quantitatively precipitated as strontium nitrate by adding an equal volume of 10% nitric acid butyl alcohol solution.

Calcium nitrate dissolves in normal butyl alcohol to the extent of 19.73% at 25° giving a solution of density 0.9427 at 25°/4° as compared with 0.8059 for the pure solvent under the same conditions. Upon the addition of nitric acid to the butyl alcohol the solubility of calcium nitrate increases rapidly being 24.85% in a 1% nitric acid butyl alcohol solution.

Upon precipitating a mixture of strontium and calcium perchlorate

* By Prof. H. H. Willard.

dissolved in normal butyl alcohol by the addition of a nitric acid-butyl alcohol solution, some calcium is ordinarily carried down by the strontium nitrate precipitate as might be expected. The method is thus seen to be attended with certain errors which however, it should be possible to eliminate.

A similar procedure for a separation of calcium and magnesium naturally suggests precipitation of the former as sulfate because of the vast difference in the aqueous solubilities of calcium and magnesium sulfates. In this case the use of methyl alcohol was found best. To test the solubility of calcium sulfate in methyl alcohol 1 cc. of a solution of the perchlorate in methyl alcohol containing 1 mg. of calcium perchlorate per cc. was added to 100 cc. of ordinary undried methyl alcohol. 0.5 cc. of 95% sulfuric acid was added to this solution of methyl alcohol containing 1 mg. of calcium perchlorate and the mixture was cooled in an ice bath for two hours. A distinct precipitate of calcium sulfate was obtained.

A saturated solution of magnesium perchlorate in methyl alcohol is not precipitated by the addition of 95% sulfuric acid.

Calcium sulfate dissolves in pure methyl alcohol to the extent of 1.0 mg. per 100 cc. The solubility of calcium sulfate in ethyl alcohol was found to be 2.0 mg. per 100 cc. There is every reason to believe that such a method for the separation of calcium from magnesium would prove successful.

